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Recent Results in a Search for Inorganic Scintillators for X- and Gamma Ray Detection*

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Abstract

We present recent results from an ongoing search for inorganic scintillators for gamma ray detection in which we measure the scintillation properties (luminous efficiency, decay time, and emission wavelength) of powdered samples excited by brief x-ray pulses. Recent promising candidates include cerium doped lutetium borate ($LuBO_3$) and the lutetium double phosphates $K_3Lu(PO_4)_2$ and $Rb_3Lu(PO_4)_2$, which have luminous intensities above 25,000 photons/MeV. In order to find scintillators that are compatible with silicon photodetectors, we have tested over 1,100 samples using a photomultiplier tube with a GaAs:Cs photocathode, which is sensitive to emissions from 200–950 nm. While many samples exhibit strong emissions in the 600–900 nm range, all have decay times that were larger than 10 μs.

I. Introduction

We have previously described [1, 2] a method for finding new scintillators by measuring the scintillation properties (luminous efficiency, decay time, and emission wavelength) of powdered samples when excited with brief x-ray pulses [3, 4, 5]. By synthesizing and testing candidate compounds as powders, the difficult task of obtaining large, optically clear samples need only be performed for the most promising compounds. To date, over 1,100 powdered samples have been measured, including both intrinsic and doped compounds. This search method has yielded several candidate materials, including cerium fluoride [6], lead tungstate [1], $LuAlO_3$:Ce [7], and the materials described herein. We are continuing this search to find materials with properties suited for gamma ray detection, which include short attenuation length, high effective atomic number, short fluorescent decay time, high luminous efficiency, and the ability to be economically formed into large, transparent pieces. We are also extending our search to cover longer emission wavelengths, as applications that utilize silicon photodiodes as optical detectors would benefit from scintillators that emit in the 550–1050 nm wavelength region. Many potentially useful materials may have been missed in previous searches because conventional bialkali photomultiplier tubes that are insensitive to emissions in this wavelength range were used.

II. Methods

Powdered samples are measured by exciting them with 20 to 30 keV, 90 ps wide x-ray pulses from the table top pulsed x-ray unit shown in figure 1 and observing their emission intensity with a sapphire windowed microchannel plate photomultiplier tube. The powdered samples are placed in a quartz cuvette 50 mm long, 5.0 mm outer diameter, with 0.37 mm wall thickness, and sealed with a plastic cap. The cuvette is placed in a holder in a light-tight box in the x-ray beam. A thin aluminum window allows the 20-30 keV x-rays to penetrate the box and excite the sample. Some of the potential fluorescent photons from the sample reach a photomultiplier tube, and its subsequent output measured. Comparison of this photomultiplier tube output to that from powders of a known, well-established scintillator (BGO) is then used to derive the emission intensity. Some samples have individual grains that are not powdered (*i.e.* ~1 micron typical dimension), but are small (0.5 mm typical dimension) crystals. This reduces their optical attenuation (as compared to a powder), and so artificially increases their measured luminosity, typically by a factor of 2–5 [2]. By recording the time difference between the x-ray pulse and the scintillation signal with the delayed coincidence method [8] (with an instrumental response time of 120 ps fwhm), the fluorescent lifetime is measured. By inserting a computer controlled monochromator between the sample and the photomultiplier tube, the emission spectrum is measured [5]. This spectrum is corrected for the wavelength dependent efficiency of the monochromator, but not of the photomultiplier tube, which has a relatively flat response (70 mA/W) between 300 and 850 nm.

To study emissions with >500 nm wavelength, we use a Hamamatsu R 943-02 photomultiplier tube with a GaAs:Cs photocathode, which has high sensitivity to emissions from 200–900 nm. The quantum efficiency and dark current (when cooled to –20° C) of this photomultiplier tube are comparable

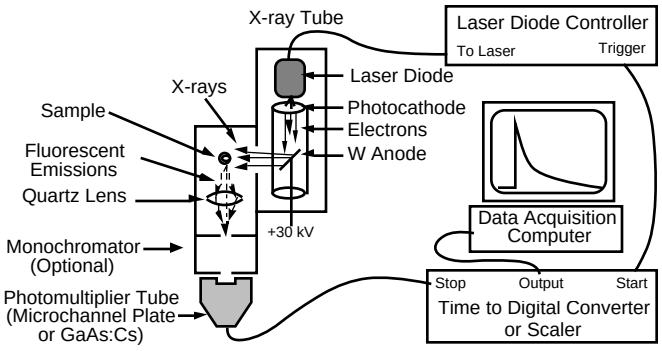

Figure 1. Measurement Apparatus. X-rays from the pulsed x-ray tube impinge on a powdered sample in a quartz cuvette, and the resulting fluorescent emissions (if any) are detected by a photomultiplier tube. The photomultiplier tube count rate measures fluorescent intensity and the delayed coincidence method is used to measure the fluorescent decay time. By inserting a monochromator into the optical path, the emission spectrum is measured.

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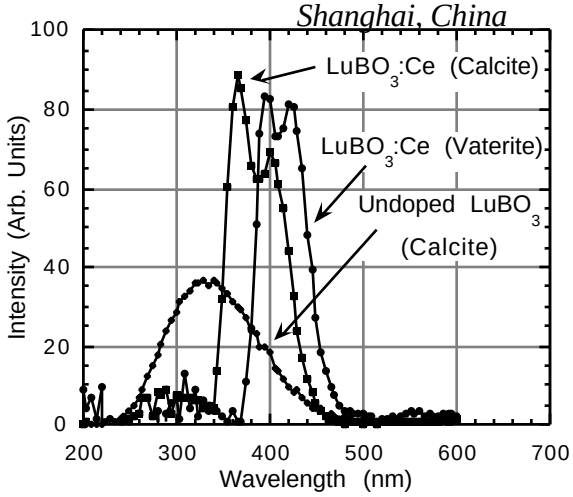

Figure 2. Emission spectra (not to scale) of lutetium borate compounds, corrected for wavelength dependence of monochromator (but not PMT) efficiency.

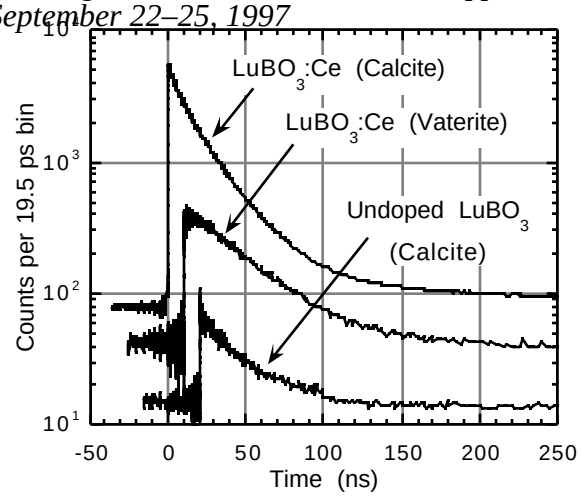

Figure 3. Decay of the lutetium borate compounds (t=0 displaced for clarity), measured with a microchannel plate photomultiplier tube.

to a bialkali photomultiplier tube at room temperature, but because of the electron optics in this design (it is a "side-on" photomultiplier tube in an "end-on" package), the single photoelectron transit time jitter is approximately 4 ns fwhm. To restrict our sensitivity to the 600–900 nm range, a pair of filters (Hoya O-54 and R-62) are placed in the optical path. A pair (rather than a single filter) was used to reduce filter fluorescence [9], and the filters were kept in the dark for a day before data collection to minimize phosphorescence.

III. Lutetium Borate

One potentially interesting compound is cerium activated lutetium borate ($LuBO_3$:Ce) [10]. This compound exists in two phases: the low temperature calcite phase (ρ=6.9 g/cm^3, stable below 1310° C) and the high temperature vaterite phase (ρ=7.4 g/cm^3, stable above 1310° C) [11]. This implies an attenuation length for 511 keV photons of 1.3 cm for the calcite phase, 1.2 cm for the vaterite phase, and a photoelectric fraction of 34% for either phase. For the vaterite phase (with 0.1% Ce), the luminous intensity is 26,000 photons per MeV, the emission spectrum has overlapping peaks centered at 395 and 425 nm (2000 cm^{-1} Stokes shift), and the decay time is fit by a single exponential component with a 39 ns decay constant. For the calcite phase (with 0.5% Ce), the luminous intensity is 27,000 photons per MeV, the emission spectrum has overlapping peaks centered at 365 and 400 nm (2750 cm^{-1} Stokes shift), and the decay time is fit by the sum of four exponential components — 10% at 9.4 ns, 69% at 23 ns, 10% at 245 ns, and 6% at 1640 ns. While the vaterite phase shows no emissions without cerium doping, undoped calcite phase material has an emission intensity of 11,000 photons per MeV, a single, broad emission peak centered at 330 nm, and a decay time that is fit by the sum of two exponentials — 60% at 30 ns and 40% at 1400 ns. Figures 2&3 show the emission spectra and decay times of these samples.

While this combination of properties is nearly ideal for gamma ray detection, $LuBO_3$ may prove difficult to produce economically in large, transparent pieces. The phase transition occurs at 1310° C (at atmospheric pressure), more than 300° C below its 1650° C melting point. Since the two phases have significantly different densities and structures, common melt-based crystal growth techniques (such as Czochralski or Bridgeman) are unlikely to be successful in producing clear, single crystals without the addition of phase stabilizing dopants. Flux growth might be used to produce good quality calcite phase crystals, but materials with the calcite structure often cleave easily, which is not desirable.

IV. Lutetium Double Phosphates

Lutetium potassium phosphate [$K_3Lu(PO_4)_2$:Ce] and lutetium rubidium phosphate [$Rb_3Lu(PO_4)_2$:Ce] are also interesting cerium activated compounds. These compounds are not listed in powder x-ray diffraction databases, and so their densities are not known. Their densities can be approximated by taking the density of a similar compound and multiplying by the formula weight ratio. Such compounds are $K_3La(PO_4)_2$ (ρ=3.63 g/cc), $K_3Ce(PO_4)_2$ (ρ=3.71 g/cc), $K_3Tb(PO_4)_2$ (ρ=3.96 g/cc) and $Rb_3La(PO_4)_2$ (ρ=4.39 g/cc). This predicts a density of 4.0 g/cc for $K_3Lu(PO_4)_2$ and 4.66 g/cc for $Rb_3Lu(PO_4)_2$, but x-ray analysis shows that the lutetium double phosphate compounds have a different unit cell, so this method is unlikely to be accurate. If, however, we assume that both compounds have a density ρ=4.0 g/cc, they would have a photoelectric fraction of 19% for the potassium compound, 18% for the rubidium compound, and an attenuation length for 511 keV photons of 2.7 cm for either compound.

These compounds are very luminous — 52,500 photons / MeV for the potassium compound and 28,200 photons / MeV for the rubidium compound. Both the decay time and emission wavelength are typical of cerium (40 ns decay time, 410 nm emission wavelength). Table 1 provides a more complete list of the scintillation properties for samples with various cerium concentrations, while figures 4&5 show the emission spectra and decay times of sample with "optimal" (0.5%) cerium concentration. The emission wavelength is centered at 410 nm, independent of compound type or dopant concentration. The emission in the undoped compounds may be due to cerium impurities in the lutetium oxide starting material.

Table 1. Properties of Double Phosphate Compounds. The measured luminous intensity (in photons per MeV) and decay times of $K_3Lu(PO_4)_2$ and $Rb_3Lu(PO_4)_2$ as a function of cerium concentration.

Compound	Cerium Fraction			
	Undoped	0.1%	0.5%	1.0%
$K_3Lu(PO_4)_2$	14,500 phot/MeV 75% @ 44 ns 25% @ 1350 ns	46,400 phot/MeV 86% @ 39 ns 14% @ 1250 ns	52,500 phot/MeV 86%% @ 37 ns 14% @ 1080 ns	19,400 phot/MeV 74% @ 40 ns 26% @ 1060ns
$Rb_3Lu(PO_4)_2$	7,400 phot/MeV 95% @ 44 ns 5% @ 1290 ns	24,600 phot/MeV 89% @ 40 ns 11% @ 1190 ns	27,100 phot/MeV 91% @ 36 ns 9% @ 920 ns	28,200 phot/MeV 84% @ 34 ns 16% @ 990 ns

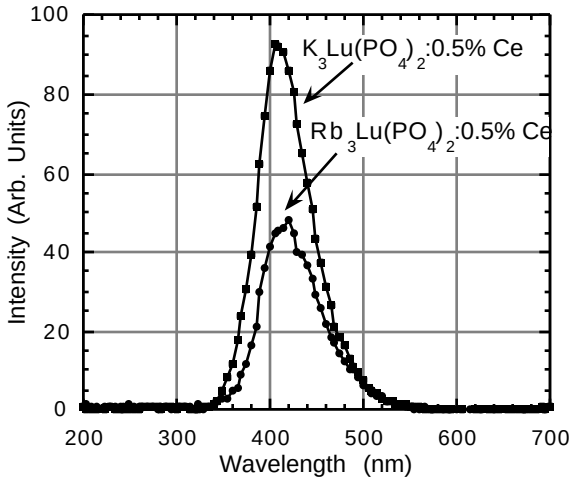

Figure 4. Emission spectra of double phosphate compounds, corrected for wavelength dependence of monochromator (but not PMT) efficiency.

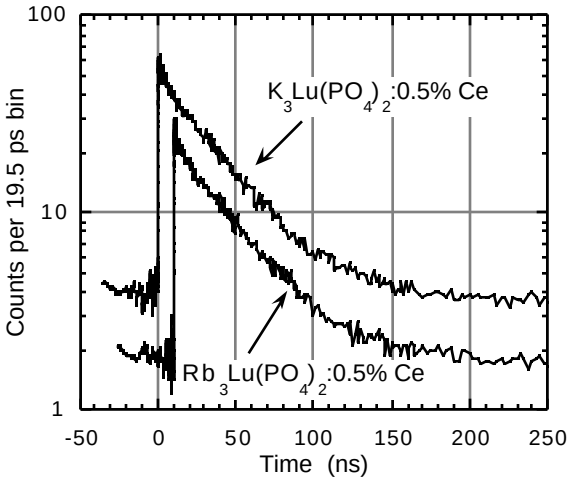

Figure 5. Decay time of the double phosphate compounds (t=0 displaced for clarity), measured with a microchannel plate photomultiplier tube.

Despite the relatively low density, these compounds have properties that are well suited for gamma ray detection. However, they may prove difficult to produce economically in large, transparent pieces. The compounds do not melt congruently, but decompose before they melt. This again makes growth by common crystal growth techniques from the melt (such as Czochralski or Bridgeman) unlikely to be successful, although flux growth may be possible.

V. Long Wavelength Scintillators

Several lanthanide and transition metal ions are known to emit at wavelengths >500 nm in suitable hosts. While most have decay lifetimes of hundreds of microseconds to many milliseconds, there are some (*e.g.* Eu^{2+}, Ce^{3+}, Fe^{3+}, and Ti^{3+}) with decay times of a few microseconds or less. We have tested all of our compounds for scintillation, and observed emission intensities comparable to commercial phosphors in the 600–900 nm range for Eu and Sm doped $LuPO_4$, $ScPO_4$, and YPO_4. Significant emissions are also observed in Tb, Dy, Er, Pr, and Tm doped phosphates, as well as several intrinsic compounds. Unfortunately, none of the compounds measured had a major scintillation decay component of 10 µs or less. Table 2 lists the luminous intensity of those compounds with a light output (in the 600–900 nm range) of ≥900 photons / MeV. Note that data for all measured compounds is available electronically in the red_luminosity.dat file via anonymous FTP to scint.lbl.gov [12].

VI. Conclusion

Several cerium activated, lutetium based scintillators that possess attractive properties for gamma ray detection have been identified and characterized. The vaterite phase of lutetium borate ($LuBO_3$:0.2% Ce) has a density of 7.4 g/cc, a luminous intensity of 26,000 photons / MeV, a decay time of 39 ns, and overlapping emission peaks at wavelengths of 395 and 425 nm. Cerium activated lutetium potassium phosphate ($K_3Lu(PO_4)_2$:0.5%Ce) has a density of ~4 g/cc, a luminous intensity of 52,500 photons / MeV, a decay time of 40 ns, and an emission wavelength of 410 nm. Despite these attractive properties, both compounds may prove difficult to fabricate in large, optically transparent pieces. Over 1,100 compounds have been examined for emissions in the 600–900 nm range, which are appropriate for readout with silicon photodiodes. While emission intensities comparable to commercial phosphors are measured in Eu and Sm doped $LuPO_4$, $ScPO_4$, and YPO_4, none of the compounds measured had a major scintillation decay component of 10 µs or less.

Table 2. Long Wavelength Luminosities. The measured luminous intensity (in photons per MeV) of the 600–900 nm emissions. Samples marked with an asterisk (*) consist of small (0.5 mm typical dimension) crystals and thus have less optical attenuation than powdered samples, yielding artificially high estimates (typical factor 2–5) for the luminosity.

Photon / MeV	Compound	Phot. /MeV	Compound
123171*	$LuPO_4$:20% Eu	2571*	YPO_4:5% Nd
103244*	$LuPO_4$:30% Eu	2497	Eu_2O_3
76099*	$LuPO_4$:~5% Eu	2468*	$LuPO_4$:0.7% Fe
61072*	$ScPO_4$:~1% Eu	2427	EuF_3
60316*	$LuPO_4$:5%Eu, 1%Gd	2418*	$BaLuYF_8$:0.2% Pr
44302*	$ScPO_4$:10% Sm	2401*	$Na_{0.4}Lu_{0.6}F_2$: 1% Nd
35728	YVO_4:Eu	2296	$Bi_2Al_4O_9$: 0.5% Ce
31543*	$ScPO_4$:3% Sm	2271*	$ScPO_4$:2% Dy
31294*	YPO_4:2% Sm	2232	$CaMoO_4$
22095*	YPO_4:?% Eu	2201	LaF_3:1% Pr, 1% Ba
15728*	$LuPO_4$:2% Sm	2157	Y_2O_3:2% Tb
14589*	$ScPO_4$:~5% Eu	2089*	$ScPO_4$:1.7% Ni
14288*	$LuPO_4$:10 % Sm	1806*	BaF_2:8.4% Ho
13067	$GdTaO_4$:Tb	1799	LaF_3:0.5% Pr
13053*	$ScPO_4$:2.9% Dy	1743*	$PbHPO_4$:5.8% Tb
12101*	YPO_4:1% Dy	1651*	$ScPO_4$:0.7% Fe
10914*	$ScPO_4$:0.7% Er	1609*	$TbPO_4$:25% Gd
10304	BaF_2:10% Eu	1526	Y_2O_3:2% Tb, 2% Eu
9316*	$LuPO_4$:10% Tb	1514	TbF_3
9280*	$ScPO_4$:10% Pr	1514	$Lu_3Al_5O_{12}$:Ce
9242*	YPO_4:2% Tm	1506*	$LaPO_4$:?% Eu
7824*	LaF_3:0.5% Pr	1444*	$LuPO_4$:2% Tm
7658*	$ScPO_4$:2.6% Pr	1427	CdF_2:1% Er
7125	$HfTiO_4$	1425	LaF_3:1% Pr
7057*	ZnS:Ag	1389	Al_2O_3
6748*	$ScPO_4$:1.7% Nd	1378	$TbCl_3$
6539	$LuTaO_4$:Tb	1304	ZnO:0.3 % Al
5284*	$ScPO_4$:0.7% V	1288	$3(Zn(OH)_2)•2(ZnCO_3)$
4776	BaF_2:5% Eu	1137	$SnSO_4$
4449*	$ScPO_4$:1% Tb	1133*	BaF_2:10% Er
4399	TiO_2	1128	BaF_2:3% Gd
4293*	$BaNb_2O_6 • SrNb_2O_6$	1088	$LuAlO_3$: 1.5% Ce
4143*	$LuPO_4$:0.63% Dy	1079*	$LuPO_4$:3.1% Nd
4029*	CdS	1073*	SbI_3
3856	$Bi_2Al_4O_9$	1069	BaF_2:1% Eu
3786	SrI_2	1054	$ThCl_4$
3446*	$ScPO_4$:2% Nd	1040	$Eu_2(CO_3)_3 • x(H_2O)$
3388*	$Y_{0.5}Gd_{0.5}PO_4$	1025*	ZnO: 0.6% In
3216*	ZnO	1017	$LuAlO_3$: 0.5% Ce
3211*	$SrTiO_3$	1011	$Bi_4Ge_3O_{12}$
3202	BaF_2:6%Gd, 0.5%Pr	1009	GdF_3:15% Ca, <1%Pr
3190*	$ScPO_4$:1.7% Yb	994	CdF_2:10% Tb
3110*	BaF_2:6%Gd, 0.2%Pr	960	ZrO_2
3060*	YPO_4:0.5% Fe	959	GdF_3:17% Sr, <1% Pr
3013*	YPO_4:1% Tb	952*	YPO_4:25% Pr
2942*	$Na_{0.4}Y_{0.6}F_2$: 1% Nd	939*	$LuPO_4$:40% Pr
2825*	$LuPO_4$:0.26% Dy	933*	$LuPO_4$:25% Pr
2823*	BaF_2:3% Gd,0.2% Pr	932	ErF_3
2713*	BaF_2:2% Gd,0.2% Pr	930	TbF_3:0.5% Ce
2690	CsI	917	$Mg_2P_2O_7 • 3(H_2O)$

VII. ACKNOWLEDGMENT

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